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Selective synthesis of carbon nanomaterials of different structures over KNO_3 catalyst

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ABSTRACT

We described a simple route for the generation of pure carbon nanomaterials (CNMs). In the decomposition of acetylene at different temperatures over KNO_3 particles, helical carbon nanofibers (HCNFs) and CNFs of low helicity (L-CNFs) are synthesized with high selectivity through the control of pyrolysis temperature. It is found that the size of KNO_3 particles is a decisive factor for the growth of CNMs. Since KNO_3 is water-soluble, it can be easily removed from the as-synthesized products through steps of water washing, and CNMs can be obtained undamaged in high purity. The approach is simple, inexpensive and environment-benign, and can be adopted for the selective production of high-purity CNMs.

1. Introduction

Carbon nanomaterials (CNMs) have received much attention since the landmark paper by Ijima [1]. Due to their unique and unprecedented physical and chemical properties, they have potential applications across many fields [2–4]. However, only some of the natural properties of CNMs are verified and related applications realized. To a large extent, the major obstacle is difficulty in obtaining high-purity CNMs [5]. There are three techniques for the production of CNMs: electric arc-discharge between two graphite electrodes, laser ablation of carbon targets, and chemical vapor deposition (CVD) via catalytic decomposition of hydrocarbons [6,7]. Common to all of the techniques, there is the involvement of transition metals, especially metals of iron-group elements (Fe, Co, Ni) and their alloys. The metals are indispensable for CNMs growth and they remain in the products [8,9]. For purification, methods such as chemical oxidation, physical separation, and those that are based on a combination of chemical and physical techniques were developed [10–14]. Despite the considerable progress, purification of CNMs is still a costly, time-consuming and environment-unfriendly business. Most undesirable of all, the purification processes are destructive and introduce defects into CNMs.

Nonlinear carbon nanospecies of different shapes such as helical carbon nanomaterials (HCNMs) were predicted to exist in the early 1990s and observed experimentally in 1994 [15–17]. Compared to the straight CNMs counterparts, HCNMs can be considered as a kind of chiral materials. It has been demonstrated that the peculiar electrical, magnetic, and mechanical properties of HCNMs could be used as lightweight materials for microwave absorption as well as utilized in nanoengineering such as electromagnetic cross-polarizing [10,18–23]. Nonetheless, HCNMs were generated only as byproducts in the synthesis of CNMs at high temperature (>700 °C) [24–26].

It was reported by Huang et al. [27] and Liu et al. [28,29] that single-walled CNTs could be synthesized by methods free of metal catalysts, and the control of catalyst size is essential. Enlightened by the idea of metal-catalyst-free growth and based on the knowhow acquired in our previous works [30–32], we investigated in the past year the use of commercial water-soluble salts as catalysts for the synthesis of CNMs [33]. Because the catalyst is water-soluble, it can be removed from CNMs through simple steps of water washing, and high-purity CNMs can be obtained easily without being damaged. In this article, we reported the use of commercial KNO_3 as catalyst for CNMs synthesis.

2. Experimental

All the materials used were commercially available and analytically pure. In order to obtain the fine powder of KNO_3, commercial KNO_3 were dissolved in deionized water. With the

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as-obtained transparent solution being kept at 80 °C for several hours, there was the formation of white powder upon water evaporation. The powder (0.1 g) was dispersed on a ceramic plate that was placed inside a quartz tube. With argon (Ar) flowing through the reaction tube, the temperature of furnace was raised from room temperature (RT) to a designated temperature (i.e. 400, 450 or 500 °C). Then Ar was cut off and acetylene was introduced into the tube at the designed temperature for 1 h. After cooling to RT in Ar naturally, a certain amount of sample (black in color) could be collected in the ceramic plate, and the products collected are denoted hereinafter as C-400, C-450 and C-500, respectively. Keeping the amounts of catalyst equal, the experimental result indicated that the yield of C-450 and C-400 was much larger than that of C-500. Averagely, ca. 0.27 g of C-400 could be collected in the ceramic plate. It was observed that the products were hydroscopic as water presence was observed after having the products exposed to air for only a few minutes.

The samples were examined at room temperature (RT) for phase identification over an X-ray powder diffractometer (XRD) using CuKα radiation (model D/Max-RA, Rigaku). Raman spectroscopic investigations were performed using a Jobin-Yvon Labram HR800 instrument with 514.5 nm Ar^+ laser excitation. Thermoanalysis was carried out on a Thermal Analysis System (Perkin Elmer TGA7 series) with ca. 5.0 mg of sample being heated in Ar at a rate of 10 °C/min. The composition of the samples was analyzed by induced couple plasma (ICP) spectrometry (Jarrell-Ash, USA). The morphologies of the samples were examined over a transmission electron microscope (TEM, model JEOL-2010, Japan) operated at an accelerating voltage of 120 kV as well as a field-emission scanning electron microscope (FE-SEM) (model FEI Sirion 200) operated at an accelerating voltage of 5 kV.

3. Results and discussion

We heated the fine powder of KNO_3 (denoted hereinafter as C1) in Ar from RT to 400, 450 or 500 °C, and obtained samples that are denoted hereinafter as C2, C3 and C4, respectively. These catalysts were used for the production of C-400, C-450 and C-500, respectively. Fig. 1a shows the TGA curve of KNO_3. One can see the former weight loss (ca. 0.6 wt%) (as indicated by I process) attributable to thermal volatilization of KNO_3 in the 289–522 °C range. And the later weight loss (II process) should be related to the decomposition of KNO_3. Similar phenomenon was observed over the C1, C2, C3 and C4 samples. The XRD patterns of C1, C2, C3 and C4 are shown in Fig. 1b. Disregard the slight variation in intensity, all of the diffraction peaks can be indexed to KNO_3, which is very close to the literature value (JCPDS no.74-2055). The results confirm that C1, C2, C3 and C4 are KNO_3 of single-phase. Shown in Fig. 1c is the XRD pattern of C-450 which is characteristic of graphitic carbon. There is no detection of KNO_3, plausibly due to the low KNO_3 content in C-450 as inferred in the experimental result (calculated amount of KNO_3 in C-450 is 0.04 wt%) and the water-soluble property of KNO_3. The graphite property of C-450 can be confirmed by the results of Raman investigation. The Raman spectrum (Fig. 1d) of C-450 exhibits two peaks. The one (called D band) at 1326.5 cm^{-1} is associated with the presence of amorphous carbon and defects in graphene sheets. The peak at 1606.0 cm^{-1} (called G band, originates from the in-plane stretching mode of the graphene sheets) is indicative of graphitic layers of high crystallinity. The intensity ratio of the D and the G band (I_D/I_G) is commonly used to characterize the crystallinity of CNMs. In our study, an I_D/I_G of ca. 0.80 was recorded for C-450, reflecting its high crystallinity.

Shown in Fig. 2 are the FE-SEM and TEM images of C-400. There is a large amount of long and uniform CNFs of low helicity (Fig. 2a–c). Hereinafter, we denoted this sample as L-HCNFs (low-helicity CNFs). The selectivity to carbon species was determined statistically based on the number of counts of CNMs at different regions of the TEM and FE-SEM images, and selectivity to L-HCNFs in the case of C-400 was ca. 95%. As shown in Fig. 2d, there is no detection of hollow tubes in the TEM images. The TEM and FESEM images show that the length of L-HCNFs ranges from tens to hundreds of micrometers, and the diameter of CNFs is rather uniform (average diameter: ca. 50 nm). As indicated by the black arrows in Fig. 2a, catalyst particles of different sizes can be detected throughout the sample. In the TEM observation, it is

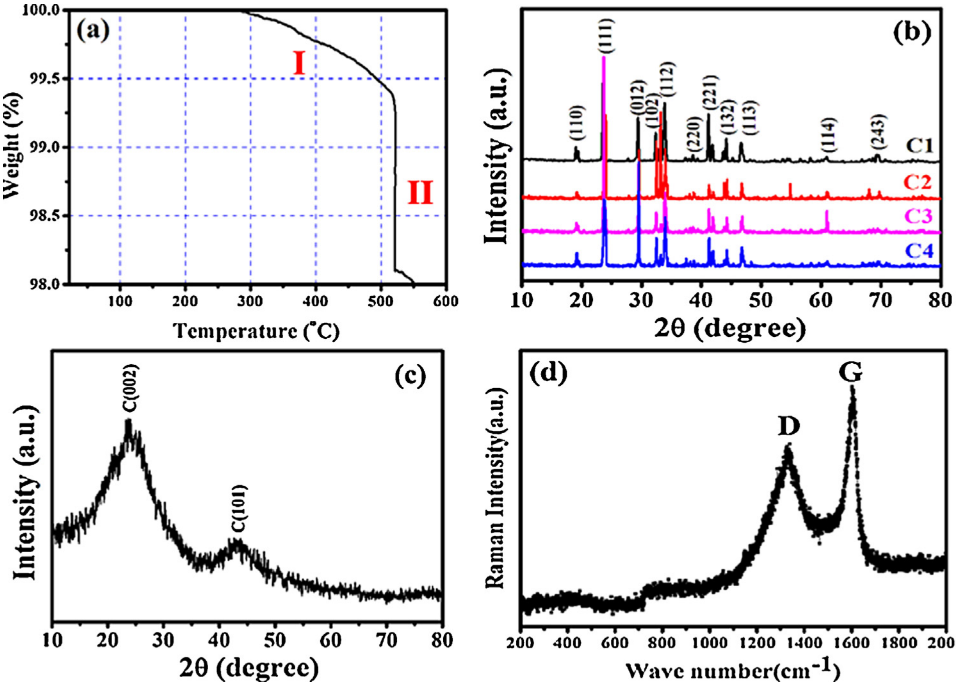

Fig. 1. (a) TGA curve of KNO_3, (b) XRD patterns of C1, C2, C3 and C4, (c) XRD pattern of C-450, and (d) Raman spectrum of C-450.